

Imaging Electron Wave Functions of Quantized Energy Levels in Carbon Nanotubes

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Abstract

Carbon nanotubes provide a unique system to study one-dimensional quantization phenomena. Scanning tunneling microscopy is used to observe the electronic wave functions that correspond to quantized energy levels in short metallic carbon nanotubes. Discrete electron waves are apparent from periodic oscillations in the differential conductance as a function of the position along the tube axis, with a period that differs from that of the atomic lattice. Wave functions can be observed for several electron states at adjacent discrete energies. The measured wavelengths are in good agreement with the calculated Fermi wavelength for armchair nanotubes.

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Carbon nanotubes are molecular wires that exhibit fascinating electronic properties [1.]. Electrons in these cylindrical fullerenes are confined in the radial and circumferential directions and can only propagate in the direction of the tube axis. Nanotubes are therefore interesting systems for studying the quantum behavior of electrons in one dimension (1D). Limiting the length of a carbon nanotube leads to a 'particle-in-a-box' quantization of the energy levels. Such discrete energy levels have been observed in transport experiments on individual nanotubes and ropes [2.,3.]. The electron wave functions corresponding to these discrete states can in principle be imaged by Scanning Tunneling Microscopy (STM). The well-known STM work on quantum corrals demonstrated the possibility to directly image wave patterns in the local density of states of a 2D metal surface [4.]. Here, we apply this technique to map out the wave functions of single molecular orbitals in short metallic carbon nanotubes. Electronic wave functions are apparent from periodic oscillations in the low-bias differential conductance along the tube axis. To our knowledge, this is the first time that wave functions of discrete electron states have been imaged in a molecular wire.

Previous STM spectroscopy studies were done at a large (~ 2 eV) energy scale to investigate the bandstructure of nanotubes [5.,6.]. These experiments confirmed the prediction [7.] that carbon nanotubes can be semiconducting or metallic depending on the tube diameter and the chiral angle between the tube axis and hexagon rows in the atomic lattice. In this paper we focus on the low-energy (~ 0.1 eV) features of short metallic nanotubes which exhibit quantum size effects. Single-wall nanotubes with a diameter of about 1.4 nm were deposited on Au(111) substrates [5.,8.]. On most tubes we were able to obtain STM images with atomic resolution [5.] which allows to determine the chiral angle and diameter of the tubes [9.]. The nanotube of Fig. 1B is identified as an 'armchair' tube from the good fit between the observed hexagon structure and the overlay of the graphene lattice. Armchair tubes have a nonchiral structure because the hexagon rows are parallel to the tube axis. This type of tubes has metallic properties [7.]. Current-voltage $I(V)$ characteristics measured up to ± 0.5 V on the armchair tube of Fig. 1B indeed demonstrate the simple linear behavior expected for a metallic tube. Such $I(V)$ measurements are done by keeping the STM tip

stationary above the nanotube, switching off the feedback, and recording the current as a function of the voltage applied to the sample. In all our experiments the STM is operated at 4.2 K [10.].

In the experiments reported here, the armchair tube of Fig. 1B was shortened to a length of about 30 nm. This was achieved by locally cutting the tube by applying a voltage pulse of +5 V to the STM tip at a position on the tube located 30 nm from its end [11.]. STM spectroscopy was then carried out near the middle of the short tube. $I(V)$ curves on the shortened nanotube show a step-like behavior (Fig. 2A), which we ascribe to quantum size effects. Steps in $I(V)$ correspond to quantized energy levels entering the bias window upon increasing the voltage. Current steps at a voltage V thus correspond to discrete electron states at energy $E = E_F + \alpha eV$, with E_F the Fermi energy, e the electron charge, and $\alpha \simeq 1$ [12.]. The experimentally observed width of the current plateaus between the steps ranges from 0.05 V to 0.09 V. The plateau width is determined by the total energy to add an electron to the tube. This addition energy consists of a combination of finite-size level splitting and the Coulomb charging energy that is due to the small capacitance of the tube. A simple estimate for the energy level splitting for a tube of length $L = 30$ nm is given by $\Delta E = \hbar v_F / 2L = 0.06$ eV, where $v_F = 8.1 \cdot 10^5$ m/s is the Fermi velocity and \hbar is Planck's constant. The capacitance of a nanotube lying on a metallic substrate can be approximated by the formula for a metallic wire parallel to a conducting plane, $C = 2\pi\epsilon_0 L / \ln[(d + (d^2 - R^2)^{1/2})/R]$ [13.], where $\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m, d is the distance from the wire axis to the plane and $R = 0.65$ nm is the wire radius. Estimating $d \approx 0.9$ nm gives $C \approx 2.0$ aF, which yields a charging energy $E_c = e^2/C = 0.08$ eV. Both numbers are in the same range as the observed plateau width. Since the charging energy and level splitting are of about equal magnitude, an irregular step spacing in the $I(V)$ curve is expected [14.]. For this report, the main point is that each step corresponds to a discrete energy level entering the bias window.

The central result of our experiments is that the tunneling conductance measured for such discrete states is found to oscillate along the length direction of the nanotube with a

period different from the atomic lattice constant. $I(V)$ spectroscopy curves were obtained at different locations on top of the nanotube along a line parallel to the tube axis in constant-current mode. At every point, spaced 23 pm apart, the feedback was switched off to take an $I(V)$ curve, starting at the bias voltage used for feedback in the constant-current mode. Figure 2A shows several $I(V)$ curves obtained in this way at different positions. The current displays a clear variation between maximum (dashed curves) and minimum values (solid curves) for negative bias voltage. Peaks in the differential conductance dI/dV (Fig. 2B) appear at the voltage positions of current steps in the $I(V)$ curves. The height of the dI/dV peaks varies periodically with position x along the tube axis, as shown in Fig. 2C. The period of these oscillations in the differential conductance is about 0.4 nm, which clearly differs from the lattice constant of 0.25 nm. The periodic variation of dI/dV versus x can - as discussed below in detail - be attributed to the electronic wave functions in the nanotube.

The wave functions of several adjacent energy levels can be displayed simultaneously by plotting the differential conductance dI/dV as a function of the voltage and the position x along the tube (Fig. 3A). Wave patterns can be observed for 4 different energy levels appearing at bias voltages 0.11 V, 0.04 V, 0.00 V and -0.05 V [15.]. At each level a horizontal row of about 7 maxima is resolved in dI/dV as a function of position x along the tube (see Fig. 3B for the 1D spatial profile of the wave functions belonging to these states). The experimental quantity dI/dV is a measure for the squared amplitude of the quantized electron wave function $|\psi(E, x)|^2$ [16.]. The curves in Fig. 3B are fitted with a function of the form $dI/dV = A \sin^2(2\pi x/\lambda + \phi) + B$, which represents a simple trial function for $|\psi(E, x)|^2$. The separation of about 0.4 nm between peaks in dI/dV corresponds to half the wavelength λ , because dI/dV measures the square of the wave function. The wavelengths obtained from the fitting procedure vary from 0.66 to 0.76 nm (Fig. 3B). Other measurements on the same tube reproduced values for λ in the range of 0.65 – 0.8 nm. From repeated spectroscopy measurements such as Fig. 3A on the same tube, we estimate the error in the wavelength to be about 0.02 nm. Note that the dI/dV maxima in Fig. 3A occur at different positions x for the different horizontal rows. This excludes many experimental artifacts such as for

example oscillations in the STM and provides compelling evidence for the interpretation in terms of standing electron waves. Typically only a small number (~ 4) of discrete levels were observed around zero bias. At larger bias voltages (beyond the images shown here), peaks in $dI(V)/dV$ could no longer be discerned clearly. At these voltages the broadening of energy states apparently exceeds their separation. Similar electron waves with a wavelength of about 0.7 nm were also observed in a number of other shortened metallic nanotubes. On shortened semiconducting nanotubes the level splitting could not be resolved and attempts to measure electron waves were unsuccessful. A small energy level splitting is indeed expected for semiconducting tubes since here the Fermi energy is located at the top of a band [5.].

Figure 3C shows the topographic height profile from the constant-current measurement at +0.3 V, which clearly has a different periodicity from that observed in dI/dV (Fig. 3B). The period of 0.25 nm is in agreement with the atomic lattice constant $a_0 = 0.246$ nm for an armchair nanotube. Apparently we image the atomic corrugation at high bias voltage. Simultaneously, $I(V)$ spectroscopy curves are measured at every point (Fig. 3B and C), starting at the set-point used for feedback (100 pA and +0.3 V). As a result from maintaining feedback at this voltage, the lattice periodicity is largely compensated because the STM tip follows the atomic corrugation, which makes it possible to resolve the quantized electron waves in Fig. 3B and C [16.].

Discrete levels are probed at energies near the Fermi energy E_F , and therefore the wavelength of the electron waves is close to the Fermi wavelength λ_F . Electronic bandstructure calculations [1.,7.] for armchair tubes yield two bands near E_F with a linear energy dispersion $E(k) = E_F \pm \hbar v_F(k - k_F)$, where $\hbar = h/2\pi$, $k = 2\pi/\lambda$ is the wave vector, and $k_F = 2\pi/\lambda_F$ is the Fermi wave vector. In undoped nanotubes, the two bands cross at the Fermi energy where $k = k_F = 2\pi/3a_0$. This yields $\lambda_F = 3a_0 = 0.74$ nm, independent of the length of the tube. For nanotubes on Au(111) however, E_F is shifted away from the crossing point to lower energy by $\delta E = 0.3$ eV. This is due to charge transfer as a result of a difference in workfunction with the underlying substrate [5.]. This shifts k_F to $k_F \pm \delta k$ with

$\delta k = \delta E / \hbar v_F$, and λ_F thus becomes $\frac{2\pi}{k_F \pm \delta k} = 0.69 \text{ nm (+)} \text{ or } 0.79 \text{ nm (-)}$. The experimentally observed wavelengths (Fig. 3B) correspond well to the theoretical values, confirming the predicted band structure with two linear bands crossing near E_F . This result provides quantitative evidence for our interpretation of the oscillations in dI/dV in terms of wave functions of discrete electron states.

A short metallic nanotube resembles the textbook model for a particle in a 1D box. For a discrete energy state with quantum number n , the corresponding wavelength $\lambda_n = 2L/n$. The observed wavelength is much smaller than the tube length, in accordance with the fact that the number of electrons within one nanotube band is large ($n \sim 10^2$). The wavelength will therefore vary only slightly ($\lambda_n/n \sim 0.01 \text{ nm}$) for adjacent discrete energy levels in one band.

The measurements reported here are technically challenging because they require a large series of reproducible $I(V)$ curves. Occasionally, we were able to resolve some of the spatial structure in the wave function at a length scale smaller than the Fermi wavelength, as shown in Fig. 4A. In this scan the peak spacing is nonequidistant, leading to an apparent ‘pairing’ of peaks. This feature indicates that the wave function does not conform to a simple sinusoidal form. Recent calculations by Rubio *et al.* [17.] indicate a nontrivial spatial variation of the nodes in the wave function of discrete electron states in the direction perpendicular to the tube axis (compare Fig. 4B). Line profiles can either show pairing or an equidistant peak spacing depending on the exact position of the line scan. The observation of pairing confirms that the relevant period in the line scans is the distance between next-nearest-neighbor peaks.

Our experiments demonstrate that individual wave functions corresponding to the quantized energy levels in a short metallic nanotube can be resolved because of the large energy level splitting. The technique for recording the wave periodicity at different energy states provides a tool for further exploration of the dispersion relation in nanotubes. Future work will include similar experiments on nanotubes with various chiral angles. The methodology presented in this paper also opens up the possibility of obtaining full 2D spatial maps of the

electron wave functions in carbon nanotubes.

Figure captions

Fig. 1. STM topographic images of individual single-wall carbon nanotubes. **(A)** Example of a nanotube which has been shortened by applying a voltage pulse to the STM tip above the tube [11.]. **(B)** Atomically resolved image of an armchair nanotube. The arrow denotes the direction of the tube axis. This nanotube can be identified as armchair-type because the hexagon rows run parallel to the direction of the tube axis (cf. overlay of the graphene lattice). The tube diameter is 1.3 nm. This image has been taken before the tube was shortened to 30 nm. Feedback parameters are $V = 0.1$ V, $I = 20$ pA. Images were taken in constant-current mode.

Fig. 2. STM spectroscopy measurements on a 30 nm long armchair tube. **(A)** Current-voltage $I(V)$ characteristics on the tube shown in Fig. 1B, taken at positions about 0.18 nm apart [data points 1 to 4 in (C)] on a straight line along the tube axis. Current steps correspond to discrete energy states entering the bias window. **(B)** Differential conductance dI/dV versus V , as calculated from the $I(V)$ curves. Peaks appear at the voltage positions of current steps in the $I(V)$ curves. **(C)** Differential conductance dI/dV as a function of position along the tube. Data was taken at a bias voltage of -0.08 V. Data points 1 to 4 indicate the positions at which the four $I(V)$ curves plotted in (A) and dI/dV curves in (B) were obtained.

Fig. 3. Spectroscopy and topography line scans along the nanotube which show electron wave functions of discrete electron states as well as the atomic lattice. **(A)** Differential conductance dI/dV (in color scale) against the bias voltage (y -axis) and the position on a straight line along the tube (x -axis). This plot results from about 100 $I(V)$ curves taken at positions about 23 pm apart along the tube axis. Electron wave functions of 4 different energy levels are observed as periodic variations in dI/dV along the tube at voltages of 0.11 V, 0.04 V, 0.00 V and -0.05 V. A horizontal row of about 7 dI/dV maxima is observed

at each energy level. Note that the exact voltages at which the peaks in dI/dV appear in Fig. 2 and Fig. 3A are different [15.]. **(B)** dI/dV profiles at the 4 resolved energy levels. Fits of the function $dI/dV = A\sin^2(2\pi x/\lambda + \phi) + B$ are plotted as dashed curves. The resulting wavelengths λ are given above the curves on the right. Curves are vertically offset for clarity. **(C)** Topographic height profile $z(x)$ of the nanotube. STM topographic imaging and spectroscopy was performed simultaneously by scanning the tip along the tube and recording both the tip height (with feedback on) and $I(V)$ spectroscopy curves (feedback off). Feedback parameters are $V = 0.3$ V and $I = 100$ pA.

Fig. 4. Pairing of conductance peaks. **(A)** Spectroscopy line scan where pairing of dI/dV maxima can be observed. Neighboring peaks are nonequidistant, indicating a nonsinusoidal wave function. The distance between next-nearest-neighbor peaks is approximately 0.75 nm which agrees with the Fermi wavelength. **(B)** Schematic of a possible arrangement of lobes of the wave function of a single molecular orbital. In a line scan along the blue line, peaks in dI/dV will be equidistant, whereas pairing will occur if a line scan is carried out along the red line.

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12. The applied voltage is in principle divided into a part that drops over the tunnel gap and a part that drops between the nanotube and the substrate. The ratio α between these voltages is determined by the capacitance ratio. Because the capacitance between nanotube and substrate is much larger than that between the nanotube and the STM tip, the voltage will drop almost entirely over the tunnel gap, and accordingly α has a value close to 1.
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15. Note that the exact voltages at which the peaks in dI/dV appear in Fig. 2 and Fig. 3A are different. This can be attributed to variations in the offset charge caused by trapping of charge in the environment of the tube, as is well known in Coulomb charging phenomena (see e.g. R. Wilkins, R. C. Jaclevic, *Phys. Rev. Lett.* **63**, 801 (1989); J. G. A. Dubois, E. N. G. Verheijen, J. W. Gerritsen. H. Van Kempen, *Phys. Rev. B* **48**, 11260

(1993)). Variation of the offset charge may change the Coulomb gap and thus shift the exact voltage at which the discrete levels of the tube appear in the $I(V)$ measurements. In fact, switching of offset charges was observed in some of our line scans. This effect is irrelevant for the observation reported here, which are the periodic oscillations in the differential conductance of discrete energy levels.

16. The total wavefunction is in fact defined by the atomic lattice potential modulated with a standing wave profile resulting from the confinement in the length direction. Because the STM tip follows the atomic corrugation by scanning in constant-current mode at a high bias voltage, the lattice periodicity is largely compensated so that the standing waves can be resolved in the spectroscopy measurements for several discrete states at low bias.
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